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STUDIES OF POLYMERS FOR SHOCK ABSORPTION APPLICATIONS

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ABSTRACT

The purpose of this study was to evaluate polymers with potential shock damping properties. Many soft polyurethane elastomers were prepared in the laboratory and evaluated by thermal and mechanical analysis; these include mostly poly(propylene oxide) and polythioether-based elastomers prepared with toluene diisocyanate. Tri- and tetrafunctional chain extenders were used in all cases, as well as some unusual secondary diamines. The objective was to soften the polymers, disorganize the hard phase, and broaden the soft segment glass transition temperature while still allowing a rather broad use temperature. Comparisons were made to commercially available shock absorbing polymers. The synthesis of the polyurethanes is discussed in detail and the results of characterization of all of the polymers are described. The polymers exhibit T_g 's ranging from -68°C to -19°C , final softening temperatures between 115°C and 246°C , Shore A hardness values ranging from 13 to 87, tensile strengths of 0.7 MPa to 20 MPa and elongations of 175% to 2900%. Several display low Bashore rebound values in the temperature range of interest. Dynamic mechanical data were extrapolated to high frequency through the assembly of master curves and revealed that the polymers evaluated probably would exhibit good high frequency shock absorbing properties at room temperature or somewhat above room temperature, but that they would not display satisfactory behavior at temperatures significantly below room temperature.

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INTRODUCTION

Polymers for potential shock absorption applications are examined in the research reported here. Many polyurethanes have been prepared in our laboratory based upon starting materials which were likely to provide shock absorption over a wide temperature range. These include mainly poly(propylene oxide) (PPG) and polythioether (PTE) based elastomers prepared with toluene diisocyanate (TDI). Tri- and tetrafunctional chain extenders were used in many cases, as well as some unusual secondary diamines. The objective was to soften the polymers, disorganize the hard phase, and broaden the soft segment glass transition temperature while still allowing a rather broad use temperature range. Crosslinking of the hard phase often leads to high softening temperatures for polyurethane elastomers. A list of starting materials for the polyurethanes is provided in Table 1. Commercially available polyurethane formulations Sorbothane and Isoloss are included. Other products examined were the poly(vinyl chloride) (PVC) based Isodamp, a polyphosphazene Eypel F compound, and a butyl rubber compound based upon Exxon HT 1066. Primarily, soft polymers were considered since the commercially available shock absorbing polymers were typically soft.

Table 1. LIST OF STARTING MATERIALS FOR THE SYNTHESIZED POLYURETHANES

Materials	Source
<u>Diisocyanate</u>	
TDI (80/20 2,4/2,6)	Olin, Stamford, CT
<u>Polyols</u>	
PTMO 2000	Quaker Oats, Chicago, IL
Olin Poly G 55-56 EO terminated* MW 1975	Olin, Stamford, CT
Olin Poly G 26-37 MW 2976	
Olin Poly G 20-56 MW 2007	
Olin Poly G 20-112 MW 1012	
Niax PPG E-351 EO terminated* MW 2903	Union Carbide, Danbury, CT
Permapol P-3 880 EW 964 or 1020	Products Res. and Chem., Glendale, CA
Permapol P-3 820 EW 610	
<u>Chain Extenders</u>	
Unilink 4100; Unilink 4200	UOP, Inc., Des Plaines, IL
Unilink 4130; Unilink 4230	
Quadrol	BASF, Parsippany, NJ
Isonol 93	Dow Chemical, Midland, MI
Trimethylolpropane	Aldrich, Milwaukee, WI
1,4-Butanediol	
<u>Catalysts</u>	
Dibutyltin Dilaurate	M&T Rahway, NJ
Coscat 83	Cosan Chemical Corp., Carlstadt, NJ
Oleic Acid	J.T. Baker, Phillipsburg, NJ
<u>Prepolymers</u>	
Andur 9000AP EW 808	Anderson Development Co., Adrian, MI
Polaroid XPE-30 EW 536	Polaroid Corp., Assonet, MA

*These polyols have poly(propylene oxide) blocks and are terminated by shorter poly(ethylene oxide) blocks to provide primary hydroxy groups for faster reaction with diisocyanate.

The synthesis of the polyurethanes will be discussed in detail, along with the results of characterization by thermomechanical analysis, differential scanning calorimetry (DSC), Shore A hardness, Bashore rebound resilience, stress-strain analysis, and dynamic mechanical analysis.

The suitability of the materials for shock damping applications will also be discussed. Caution is required in the choice of a polymeric material for a shock damping application because most of the methods available to polymer scientists do not simulate shock impact in which the frequency and the amplitude of the shock waves can be very high. The purpose of this study is to compare, evaluate, and to suggest new polyurethanes which should be tested in the actual application.

EXPERIMENTAL

Materials

The starting materials for the polyurethanes prepared in the laboratory are listed in Table 1 and selected chemical compounds are shown in Figure 1. The molecular weights of the polyols are listed and were obtained from the hydroxyl number supplied by the manufacturer. The two Permapols differed in that the 820 has a functionality of 2.2 and an equivalent weight of 610, and the 880 has a functionality of 2.0 and equivalent weights of 964 and 1020 for the two batches used. The Permapols had acid numbers of about 2.6 mg KOH/g. Only TDI was used in the study reported here. Chain extenders included the Unilink compounds and other tri- and tetrafunctional chain extenders such as Isonol 93 and Quadrol listed in the table. The Unilink 4130 and 4230 are mixtures of Quadrol and 4100 or 4200, respectively, being 30 equivalent percent Quadrol and the remainder one of the secondary diamines. Isonol 93 is not a pure compound and the batch used had an equivalent weight of 90.8 compared to 88.7 for the pure compound.

The XPE-30 prepolymer from Polaroid is based upon PTMO 650 and TDI and had an equivalent weight of 536.4. Andur 9000AP from Anderson Development Company is a TDI-based polyether prepolymer with % NCO = 5.2 and equivalent weight of 807.7.

Other polymers evaluated included either commercially available shock absorbing polymers or nonpolyurethane polymers reported to have good damping characteristics. Isodamp C-1002 is manufactured by the E-A-R Division of Cabot Corporation and is a plasticized poly(vinyl chloride). A report of its composition and properties has appeared.¹ Isoless HD is a polyurethane-based damping material also manufactured by E-A-R. Sorbothane is a polyurethane-based material manufactured by Sorbothane, Incorporated. Eypel F elastomer compound 3301 is a fluoroalkoxy phosphazene prepared for vibration damping by Ethyl Corporation. The butyl rubber compound² used in this study was based upon Butyl HT 1066, a chlorobutyl elastomer from Exxon. It was formulated as a standard rubber compound for other work and was not optimized for its damping characteristics. All of the polymers which were evaluated are listed in Table 2.

1. BYRNE, C. A., and ZUKAS, W. X. *Shock Absorbing Polymers: Chemical Analysis and Characterization*. Polymeric Materials Science and Engineering Proceedings, v. 61, 1989, p. 560.
2. WILDE, A. *Standard Rubbers for Chemical Defense Research*. Volume I: Formulations and Properties. U.S. Army Materials Technology Laboratory, MTL TR 89-5, January 1989.

Table 2. POLYMERS EVALUATED

Sample Number	Chemical Composition*
1	3.0 TDI-1 PTMO 2033-1.5 Unilink 4200-0.33 Isonol 93
2	2.0 TDI-1.0 PPG 1975-0.67 Isonol 93
3	2.0 TDI-1.0 PPG 1975-0.67 BD-0.33 TMP T12
4	2.0 TDI-1.0 PPG 1975-2.0 EQ Unilink 4130
5	3.0 TDI-1.0 PPG 2903-1.33 TMP
6	3.0 TDI-1.0 PPG 2903-1.5 BD-0.33 TMP
7	3.0 TDI-1.0 PPG 2007-1.33 TMP
8	3.0 TDI-1.0 PPG 2007-1.33 BD-0.44 TMP
9	3.0 TDI-1.0 PPG 2007-4.0 EQ Unilink 4230
10	3.0 TDI-1.0 PPG 1012-4.0 EQ Unilink 4230
11	2.0 TDI-1.0 PPG 1012-2.0 EQ Unilink 4130
12	2.0 TDI-1.0 PPG 1012-2.0 EQ Unilink 4230
13	3.0 TDI-2.0 EQ PermP3-820 [†] -1.33 BD-0.44 TMP
14	2.0 TDI-2.0 EQ PermP3-820-0.67 BD-0.22 TMP
15	2.0 TDI-2.0 EQ PermP3-820-0.67 Isonol 93
16	2.0 TDI-2.0 EQ PermP3-820-2.0 EQ Unilink 4130
17	3.0 TDI-1.0 PermP3-880-1.33 BD-0.44 TMP
18	2.0 TDI-1.0 PermP3-880-0.67 TMP
19	1.0 Andur 9000AP-1.0 EQ Unilink 4130
20	1.0 XPE-30-0.8 BD-0.2 EQ Isonol 93
21	Isodamp PVC
22	Isoloss polyurethane
23	Sorbothane polyurethane
24	Eypel F
25	Butyl rubber

*Moles, except where equivalent weights (EQ) are indicated.

[†]The Permopol 820 has a functionality of 2.2 and so the equivalent weights are used for those samples.

Synthesis

Polymer Sample 1 prepared with poly(tetramethylene oxide) was prepared using the prepolymer technique at 100°C throughout at an NCO/OH = 1.0. The prepolymer step took one and one-half hours and the chain extension 16 hours in the mold.

Polymer Samples 2 through 6 prepared with the ethylene oxide end-capped propylene glycol were also made using the prepolymer technique at an NCO/OH = 1.0. The amount of T-12 catalyst solution required was 2 μ l /g prepolymer of 4% by weight dibutyl tin dilaurate, which was added during the prepolymer step. The prepolymer step took one and one-half hours and the chain extension 16 hours in the mold at 100°C throughout.

For Samples 7 through 12 prepared with hydroxy terminated poly(propylene oxide), the prepolymer technique was also used at an NCO/OH = 1.0. Polyol and diisocyanate were heated at 100°C for about two hours and then titrated to assure that the theoretical amount of isocyanate group remained (within 0.3%). T-12 catalyst ($2 \mu\text{l/g}$ polymer) was added at the chain extension step. The polymers were cured in the mold for 16 hours. This procedure worked well for samples which did not contain secondary amine groups such as 1,4-butanediol, trimethylolpropane and Isonol 93. The samples prepared with the Unilink chain extenders, including those mixed with Quadrol, required another catalyst in some cases. The addition of a catalyst mixture of Coscat 83 and oleic acid (bismuth phenyl carboxylate, 0.25% by weight, oleic acid, 0.5% by weight) improved the properties of the polymers so that the generally tacky samples could be removed from the mold. This was especially true with Unilink 4130 and PPG 2007; less so with Unilink 4230. Useable samples could not be prepared with PPG 2976, except for three TDI-PPG 2976-2 EQ Unilink 4230 (not reported in Table 2), which was acceptable for testing. Samples prepared with PPG 1012 without catalyst were good quality and not very tacky.

For Samples 13 through 18, a one-step polymerization worked best due to the increased reactivity of the polyol. The Permapols were degassed at 100°C for two hours under vacuum. TDI and chain extender were preheated to 90°C to 100°C. In a polyethylene beaker, the polyol was weighed, and then the TDI was added and rapidly mixed for one minute. Chain extender was added and mixed for another minute. The thick liquid was degassed until the bubbles collapsed and was poured into a preheated mold. The samples were cured for 16 hours at 100°C. Difficulty was encountered in the preparation of bubble free samples.

Sample 19 in Table 2 was prepared by mixing equal amounts (in equivalents) of Andur 9000AP and Unilink 4130, both of which had been preheated to 100°C, degassing and curing in a preheated mold at 100°C for 16 hours. Sample 20 in Table 2 was prepared by mixing a 4:1 (in equivalents) mixture of BD with Isonol 93 with an equivalent (plus five % excess) of XPE-30. The components were preheated to 70°C, mixed, degassed, and cured in a preheated mold at 100°C for 16 hours.

Thermal Analysis

Dynamic DSC was performed on a Perkin-Elmer DSC-7 Thermal Analysis System. In the low temperature range, 150 K to 300 K, the system was purged with helium and the temperature was maintained with liquid nitrogen. Samples weighing 10 mg to 15 mg were encapsulated in stainless steel pans sealed with Viton O-rings. The heating rate was 20°C/min and the cooling rate was 40°C/min. The resulting curves were analyzed using the Perkin-Elmer 7700 Professional Computer.

Thermomechanical analysis (TMA) was performed on a Perkin-Elmer TMS-1 with a Model UU-1 temperature program controller. The samples were 1.3 mm to 1.5 mm thick; a weight of 20 g was used on the TMA probe. Samples were heated in a helium atmosphere from -100°C to the softening point of the sample at a rate of 20°C/min.

Mechanical Testing

Tensile strength measurements were made using ASTM D1708 at a rate of 2 in./min. A floor model universal testing machine from Instron was used for the tests. Bashore rebound tests were made using ASTM D2632. For testing below room temperature, the samples were conditioned for at least 30 minutes at the test temperature.

Dynamic mechanical analysis was carried out using a Rheometrics Dynamic Spectrometer, RDS-7700. The dynamic shear moduli were obtained as functions of frequency and temperature from torsional experiments on rectangular specimens approximately 50 mm long and 12 mm wide cut from sheets typically 1.5 mm thick. Samples were cooled to approximately -100°C and equilibrated at this temperature for three minutes before a frequency scan from 0.1 rad/sec to 100 rad/sec at 1% strain was carried out. Temperature was increased in 5°C steps for subsequent frequency scans to approximately 50°C. The data could be shown as moduli versus frequency at fixed temperature or as moduli versus temperature at fixed frequency. The first were used to assemble moduli master curves while the latter were used to determine the T_g 's of the elastomers.

Master curves were constructed for the dynamic shear storage modulus G' , and the dynamic shear loss modulus, G'' , over a wide range of reduced frequency. The data obtained closest to 25°C was used as the reference curve. A master curve was first constructed for the G' data with the frequency scans at the different temperatures shifted along the frequency axis until overlap was achieved. The same shift factors were used to assemble master curves for the G'' and $\tan \delta$ (G''/G') data. The assembled master curves thus represent room temperature data over a much wider frequency range than actually measured. Dynamic mechanical data were obtained on the following samples referred to by number in Table 2: 1, 4, 6, 8, 12, 15, 18, 19, 21, 22, 23, 24, and 25.

RESULTS AND DISCUSSION

In a preliminary study reported earlier, poly(tetramethylene oxide) was used to prepare all of the samples made in the laboratory.¹ Chain extenders included those in Table 1, as well as several other compounds, such as BASF Pluracol P-355 which is a mixture of higher oligomers of Quadrol and Quadrol itself. The different tetrafunctional chain extenders could not be distinguished in terms of their effect on the damping behavior of the resulting polymers. At this stage only the Bashore rebound was used to screen the polymers. Isodamp had a very low Bashore rebound of 5 at 20°C, but the value rose to 51 at -40°C. The goal was to produce polymers with low Bashore rebound values across the temperature range studied. The rebound values were not low for the PTMO-based polyurethanes from -40°C to 20°C. For this reason, the polyol used was changed to the ethylene oxide end-capped poly(propylene oxides). Because these polyols contain a large amount of ethylene oxide (45% for the sample from Olin), the Bashore rebound values again were too high throughout the temperature range considered. Klempner, Berkowski, Frisch, Hsieh, and Ting³ had reported that the polyol offering the best damping properties was poly(propylene oxide) and Samples 7 through 12 were prepared. These are terminated by a mixture of primary and secondary hydroxy groups so a catalyst was required for the preparation of many of the polymers. The novel sulfur containing polyols (Permapols) were also used because some polysulfide sealants used in the laboratory offered damping characteristics in certain constrained tests. They are interesting materials in themselves because of the presence of sulfur rather than oxygen in the chains, and additional characterization and testing of polyurethanes based upon these polyols is in progress. These happened to be samples having high acid numbers of about 2.6 mg KOH/gm. Synthesis techniques are currently being evaluated for Permapols with low acid values of 0.35 mg KOH/gm.

Many more samples than these discussed were prepared, but they are well represented by those selected for analysis and discussion. Poly(propylene oxides) and polythioethers were reacted with two or three moles of 2,4/2,6-TDI (80:20) and then chain extended with tri- or tetrafunctional compounds to disorder the hard phase. The results of characterization of

3. KLEMPNER, D., BERKOWSKI, L., FRISCH, K. C., HSIEH, K. H., and TING, R. *Interpenetrating Polymer Networks for Vibration Attenuation*. Rubber World, v. 192, no. 6, 1985, p. 16

these materials and the commercial polymers are shown in Tables 3 through 8. In Table 3, weight percent hard segments for the polymers are given and range from 17% to 50%. Generally polymers with low weight percent hard segment were prepared because softer elastomers were of interest in this study. Some of the samples were prepared with three moles of TDI instead of two even though soft polymers with low hard segment content were desired; this was because low hard segment content can lead to polyurethanes with no mechanical strength. Samples were characterized as long as they could be handled and cut up for the tests. Some were rather sticky, such as those extended with Unilink 4130.

Table 3. THE HARDNESS AND STRESS-STRAIN DATA FOR THE POLYMERS

Sample	Weight % Hard Segment	Shore A Hardness	Tensile Strength (MPa)	Elongation (%)
1	34.6	45	7.4	633
2	21.0	52	1.5	219
3	18.7	44	2.7	1478
4	21.7	13	0.8	578
5	19.4	55	1.7	243
6	19.5	34	3.0	2906
7	25.9	63	2.6	257
8	25.9	49	2.5	660
9	34.2	48	3.2	1039
10	50.7	87	18.7	774
11	35.0	45	2.4	773
12	37.5	52	5.0	952
15	30.1	56	1.7	175
16	30.9	52	1.7	502
17	26.7	42	1.7	1200
18	17.7	45	1.1	284
19	*	49	2.4	665
20	*	58	9.1	1390
21	*	65	12.2	446
22	*	57	20.7	620
23	*	16	0.7	317
24	*	29	4.7	510
25	*	75	12.6	461

*The samples were not polyurethanes or the weight percent hard segment was unknown.

The polymers are generally soft materials ranging in Shore A hardness from 13 to 87. Except for the polyurethane listed with 50% hard segment, the Isodamp and butyl rubber are the hardest materials examined, with values of 65 and 75, respectively, on the Shore A scale.

The objective is to find a polymer with a high tensile strength and a high percent elongation because the area under the stress-strain curve is the energy to break for the elastomer. A large amount of energy to break is considered important for impact performance. All of

these polymers exhibit low tensile strengths, the highest being 20.7 MPa for Isoloss and the lowest value is for Sorbothane, 0.7 MPa. All of the polymers prepared in our laboratory exhibit values in between these two. Many break at very low elongations; 175% being the lowest. Several polymers stretch to very high values; between 1000% and 2906%. Of these, Samples 3, 6, and 17 are chain extended with a mixture of 1,4-butanediol and trimethylolpropane. It is interesting to compare those with the samples chain extended with only trimethylolpropane, Samples 5, 7, and 18, which break before 300% elongation in each case. The other two samples exhibiting high elongation, Samples 9 and 20, are chain extended with Unilink 4230 and a mixture of 1,4-butanediol and Isonol 93. Samples extended with only Isonol 93 break at low elongations, just as those prepared with only trimethylolpropane. Isonol 93, as shown in Figure 1, is chemically similar to TMP and can be prepared from TMP by reaction with three moles of ethylene oxide. The chemical similarity leads to similar elongation.

The results of thermal analysis are shown in Table 4. T_g 's range from -68°C to -19°C by DSC. The thermal behavior of the polymers at high temperatures was examined only by thermomechanical analysis and the results are shown in column 4 of Table 4. Not all samples were analyzed, but of those that were Isodamp exhibits the lowest final softening temperature of 115°C ; all of the others are considerably higher. The final softening temperature for polyurethane elastomers is generally extended significantly by the use of a crosslinker in the hard segment. This does not necessarily mean that the mechanical properties are useful in the higher temperature ranges. The T_g 's obtained from the G'' curves (see Table 4) of the dynamic mechanical scans (at 10 rad/sec) are in very good agreement with those values obtained from DSC, the greatest difference (10°C) being for Sample 25, butyl rubber. A typical dynamic mechanical spectrum is shown in Figure 2 for Sample 18.

The T_g 's of the polyols used were also obtained by DSC. The pure PPGs have T_g 's of -69°C and the ethylene oxide terminated PPGs have T_g 's of -68°C . The Niox polyol also exhibits other transitions; a crystallization exotherm at -29°C followed by a poorly defined transition which could include melting and the T_g of the poly(ethylene oxide). The lower molecular weight polyol (1975) from Olin exhibits an endotherm due to soft-phase melting with a maximum temperature of about 20°C and another second order transition with a midpoint of -35°C . Only a single T_g is observed in polyurethanes prepared from these ethylene oxide terminated PPGs.

Several of the polymers in Table 2 clearly are phase mixed based upon the elevation of the T_g above that of the pure polyol. The most phase mixed are those based upon PPG 1012, which exhibit T_g 's elevated 46°C through 50°C above that of the pure polyol. The polythioether polyols exhibit T_g 's of -69°C . The Permapol 820 based polymers, which exhibit T_g 's elevated 29°C through 33°C above that of the pure polyol, are phase mixed. The polymers based upon PPG 2007 are also phase mixed, with T_g 's elevated 22°C through 28°C above that of the pure polyol. The other polyurethanes prepared in the laboratory have T_g 's elevated less than 20°C and are more phase separated. The benefit of phase mixing is that one can theoretically place the T_g of the polymer in any desired temperature range so that the $\tan \delta$ peak in the dynamic mechanical spectrum occurs in the frequency and temperature range of interest. The reason for placing $\tan \delta$ in a particular range is that a high and broad $\tan \delta$ is related to impact performance.

The results of Bashore rebound tests are shown in Table 5 for four different temperatures. Representative curves are shown in Figures 3a and 3b. These temperatures were of interest because of the U.S. Army's need for polymers with the desired mechanical properties at low temperatures. Considering that the application is a high frequency one where polymers

appear to be stiffer, the choice of low temperatures for rebound testing was appropriate. The intent of the testing was to find a polymeric material which would have a low resilience value throughout the temperature range of interest. Several polymers behaved as Isodamp did, exhibiting a very low value at 20°C and then significantly higher values at lower temperatures. Others exhibited rather low values (below approximately 20) at all the temperatures examined, such as Samples 9, 15, 16, 23, 24, and 25. One other polymer (not reported in the tables) prepared with PPG 2976 and chain extended with Unilink 4230 exhibited low Bashore rebound across the temperature range considered. It was rather sticky and not fully characterized, but perhaps should not be eliminated from consideration in further studies. The polymers prepared from the PPGs (and also the Permapols) showed different behavior depending upon which molecular weight was used to prepare the polymer because of varying degrees of phase mixing of the hard in the soft phases. PPG 1012-based polymers had low resilience at high (20°C) temperatures, while PPG 2903-based polymers exhibited low resilience at low (-40°C) temperatures. This suggests that it might be possible to lower the Bashore rebound values across the temperature range of interest by mixing the PPG polyols before synthesis.

Table 4. THE RESULTS OF THERMAL ANALYSIS

Sample	Low Temperature T _g by DSC (°C)	T _g from G'' Curve	Final Softening by TMA (°C)
1	-68	-59	165
2	-51	*	*
4	-52	-52	188
5	-58	*	*
6	-56	-57	182
7	-45	*	*
8	-40	-43	224
9	-46	*	*
11	-23	*	*
12	-19	-20	173
13	-36	*	*
15	-40	-38	246
17	-50	*	*
18	-54	-54	224
19	-26	-20	*
20	-24	*	*
21	-32	-26	115
22	-22	-16	226
23	-59	-59	145
24	-66	-59	*
25	-66	-56	*

*Not analyzed.

Table 5. THE RESULTS OF BASHORE REBOUND TESTS

Sample	-40°C	-20°C	0°C	20°C
1	30	24	22	27
2	8	9	35	70
3	6	11	37	66
4	8	11	25	28
5	10	15	32	54
6	9	11	26	45
7	40	19	14	31
8	34	17	9	31
9	19	14	13	18
10	55	28	31	9
11	45	31	12	9
12	56	35	16	6
13	45	31	27	17
14	36	21	8	14
15	14	21	11	11
16	12	17	17	14
17	28	17	16	18
18	8	12	20	39
19	41	29	9	8
20	49	38	8	16
21	51	45	15	5
22	58	57	22	10
23	18	6	9	14
24	11	7	5	16
25	23	18	12	12

The dependence of Bashore rebound behavior on T_g is shown in Table 6. The minimum value of the Bashore rebound (out of the four values obtained) is shown in the second column. This is, of course, only an approximate minimum in the curve of Bashore rebound versus temperature because measurements were taken at only four temperatures. The minima are compared with T_g 's in the third column of the table, which shows the number of degrees between the T_g and the minimum rebound test temperature. The range of $T-T_g$ is 11°C to 80°C. The reason for the wide variation is that the polymers vary widely in chemical composition. Polymer resilience is known to be lowest in the region of the T_g where the polymer is leathery.⁴ The magnitude of the transition associated with the T_g varies considerably depending upon the chemical composition of the polyurethane and the degree of phase mixing; for example, low molecular weight polyols such as PTMO 650 (when incorporated into polyurethanes) exhibit very broad, high T_g 's which are elevated as much as 80°C above T_g 's for PTMO 2000 incorporated into chemically similar polyurethanes.⁵ A large difference in the magnitude or breadth of the T_g 's was not observed in the current study for polymers prepared with different molecular weight PPGs.

4. CONANT, F. S. *Physical Testing of Vulcanizates*. Rubber Technology, M. Morton, ed., Ed. 2, chapter 5, Van Nostrand, New York, NY, 1973, p. 158-9.
5. BYRNE, C. A., McHUGH, E. A., MATTON, R. W., CLEAVES, M. A., MACK, D. P., and SCHNEIDER, N. S. U.S. Army Materials Technology Laboratory, AMMRC TR 83-57.

Table 6. DEPENDENCE OF BASHORE REBOUND ON T_g

Sample	Bashore Rebound Minimum Temperature (°C)	$T - T_g$
1	0	68
2	-40	11
4	-40	12
5	-40	18
6	-40	16
7	0	45
8	0	40
9	0	46
11	20	43
12	20	39
13	20	36
15	0/20 *	40/60 *
17	0	50
18	-40	14
19	20	46
20	0	24
21	20	52
22	20	42
23	-20	39
24	0	66
25	0/20 *	66/86 *

*The values were exactly the same at both temperatures.

Dynamic Mechanical Analysis

The ideal mechanical test for shock absorption characterization would be to examine the material under the same conditions of strain and rate of strain as the actual application. Common methods available in polymer science research laboratories for mechanical analysis do not reach the amplitude or frequency of the shock waves associated with shock impact. To circumvent this problem, techniques are utilized to make measurements where experimentally feasible, then the results are extrapolated into the regions of interest. Dynamic mechanical analysis and time/temperature superposition were utilized in this study to assemble master curves based upon reduced frequency in order to reach the high frequencies thought to better represent actual impact rates of strain. However, these measurements are made at relatively low strain which may not accurately reflect the large amplitude (high strain) shock absorbing capabilities of interest to the U.S. Army.

The actual G' and G'' data obtained over the frequency range of 0.1 rad/sec to 100 rad/sec are shown in Figures 4a and 4b, respectively, for Sample 4. The corresponding master curves derived for this sample are shown in Figures 5a and 5b for G' and G'' , respectively. Information is typically extrapolated to reduced frequencies of approximately 10^{14} rad/sec. Values for $\tan \delta$ ($= G''/G'$) were also calculated from the master curves.

This value should correlate with impact data, provided the correct frequency is used for the comparison. $\tan \delta$ represents the ratio of the energy lost during deformation to the energy stored elastically in the sample. Values for $\tan \delta$ at a given frequency and temperature should correlate with shock absorbing capability. These experiments are meant as a guideline for screening materials, realizing that the dynamic mechanical data may not necessarily correspond exactly with the impact data of interest.

Bashore rebound results have been discussed above. Resilience from this type of test is related to the ratio of energy given up on recovery from deformation to the energy required to produce the deformation.⁴ A mass is dropped on a sheet of elastomer and the amount of rebound measured, low rebound indicating a good damping material. The experiment is physically similar to half a cycle of an oscillating free vibration measurement and an equivalent frequency can be determined from a known contact time.⁶ If the maximum rate of strain calculated from the product of the angular frequency and amplitude of the dynamic test is assumed proportional to the velocity of the mass at impact in the rebound test, a frequency of approximately 1000 rad/sec is calculated to correspond to the Bashore test. Experimentally, the best agreement between the room temperature shifted $\tan \delta$ data and the Bashore rebound data at 20°C was found at 1000 rad/sec and is shown in Figure 6 for the 13 samples tested. Although some scatter is evident, generally, as $\tan \delta$ increases, a decrease in rebound is observed. This is also consistent with the data in Table 6 which show a positive deviation for the difference between the temperature of minimum Bashore rebound and T_g . The T_g values in this table were derived from an equivalent low frequency measurement and compared to the higher frequency Bashore test.

Room temperature reference $\tan \delta$ traces as a function of frequency are shown for all the samples tested in Figures 7 through 12. $\tan \delta$ values from these traces at selected frequencies are listed in Table 7. Impact of interest in a shock absorbing application is thought to correspond to frequencies in the 10^6 to 10^{10} rad/sec range. Generally, the materials with the lower T_g values have room temperature reference $\tan \delta$ maxima in the frequency region of interest; i.e., Sample 6 in Figure 7, Sample 18 in Figure 9, and Sample 25 in Figure 12. The room temperature reference data in Figures 7 through 12 generally show an expected⁷ decade shift in frequency per an approximate 7°C difference in T_g between the samples. Temperature also has an effect on the position of the data on such a plot. As the reference temperature is lowered the maximum in $\tan \delta$ will shift to correspondingly lower frequencies, as shown for Sample 18 in Figure 13. Bashore rebound actually showed lower rebound for some samples as the temperature was lowered. This corresponds to an increase in $\tan \delta$ at 1000 rad/sec as the reference temperature was decreased. Although some samples show $\tan \delta$ maxima with a room temperature reference at frequencies of 10^6 or higher, these would be shifted to lower frequencies as the reference temperature is lowered (see Figure 13). Low temperature impact at high frequency may be poor for essentially all samples since all of the samples show low $\tan \delta$ values at the frequency of interest at low reference temperatures.

Two things are desirable for impact: a high frequency maximum in $\tan \delta$ for energy absorption, and a broad peak as a function of frequency in the temperature range of interest. Based upon $\tan \delta$ values, Sample 23 has the best impact properties at the higher frequencies with $\tan \delta$ values almost twice as high as any other sample tested. Samples 4, 6, and 18 have the highest

6. KRAMER, O., and FERRY, J. D. *Dynamic Mechanical Properties*. Science and Technology of Rubber, F. R. Eirich, ed., chapter 5, Academic Press, New York, NY, 1978, p. 207.

7. NIELSEN, L. E. *Dynamic Mechanical Testing*. Mechanical Properties of Polymers, chapter 7, Van Nostrand, New York, NY, 1962, p. 162.

$\tan \delta$ values at 10^8 rad/sec of all the experimental samples and show the lowest Bashore rebound at -40°C . Samples 1, 12, and 19 all show somewhat low $\tan \delta$ values at 10^8 rad/sec and show relatively high Bashore rebound values at -40°C . These results indicate that high frequency damping will require even lower glass transition temperatures to maintain low temperature impact; this says nothing about the other physical properties which may be required of the material.

Table 7. $\tan \delta$ VALUES AT VARIOUS FREQUENCIES (RAD/SEC) FROM THE ROOM TEMPERATURE REFERENCE MASTER CURVES

Sample	10^2	10^4	10^6	10^8	10^{10}
1	0.14	0.30	0.32	0.26	0.24
4	0.16	0.39	0.93	0.75	0.38
6	0.16	0.27	0.61	0.75	0.58
8	0.07	0.63	0.71	0.43	0.24
12	0.46	0.88	0.46	0.24	0.13
15	0.11	0.53	0.62	0.39	0.24
18	0.17	0.39	0.68	0.74	0.41
19	0.40	0.69	0.39	0.20	0.11
21	0.34	0.78	0.52	0.28	0.11
22	0.16	0.92	0.62	0.26	0.11
23	0.33	1.24	1.82	0.93	0.38
24	0.05	0.78	0.93	0.26	0.07
25	0.21	0.29	0.46	0.46	0.26

The $\tan \delta$ data in Figures 7 through 12 indicate some of the structural features important for high frequency $\tan \delta$ maxima. PTMO-based materials were previously associated with high rebound.¹ Sample 1, the only PTMO-based sample tested in this study, showed the smallest $\tan \delta$ values over the entire transition region (see Figure 7) and fairly high Bashore rebound values over the temperatures tested. Comparisons between the various polyols used in this study showed the higher the molecular weight of the polyol, the higher the frequency of the $\tan \delta$ maximum (between Samples 4 and 6 in Figure 7, between Samples 8 and 12 in Figure 8, and between Samples 15 and 18 in Figure 9). A higher soft phase T_g , earlier attributed to better phase mixing in the lower molecular weight polyol, results in a lower maximum frequency in the shifted $\tan \delta$ curves. For a given molecular weight polyol, the sulfur containing Permapols (see Samples 15 and 18) gave higher frequency $\tan \delta$ maxima than the ethylene oxide end-capped PPGs (see Samples 4 and 6) and the ethylene oxide end-capped PPGs were somewhat higher than the pure PPGs (see Samples 8 and 12). A somewhat smaller $\tan \delta$ peak was observed for the Permapol-based polymers compared to either of the PPG type materials, indicating poorer damping than either at high frequencies.

The butyl sample (see Sample 25 in Figure 12) showed the highest frequency $\tan \delta$ maximum of all the commercial materials tested, but also showed the second smallest $\tan \delta$ values of all the materials tested. The low $\tan \delta$ values were expected since this material was not

specifically formulated for damping. The other commercial materials showed lower frequency $\tan \delta$ maxima. Samples 21 and 23 contained significant plasticizer levels, without which they would show even lower frequency maxima. The polyphosphazene (see Sample 24 in Figure 12) showed a unique double transition region which was also observed in the temperature representations at fixed frequency. This suggests that the Eypel F is a mixture of materials. The commercial polymers, other than the butyl compound, showed high $\tan \delta$ values compared to most of the synthesized materials with Sample 23 showing a maximum almost twice as high as any other sample. Generally, higher frequency $\tan \delta$ maxima were observed for the synthesized materials with lower $\tan \delta$ values than the commercial materials.

Inherently, modulus should be important to impact resistance. A Newtonian fluid has an infinite $\tan \delta$ value, but no structural properties. Values for G'' from room temperature reference master curves at selected frequencies are listed in Table 8. A higher value generally corresponds to a lower Bashore rebound. Samples 12 and 21 have the highest G'' values at 10^4 rad/sec and the lowest 20°C Bashore rebound. However, the agreement between G'' data and Bashore rebound shows much more scatter than $\tan \delta$ data previously discussed. Since a step change in storage modulus occurs in the glass transition region, correlation with Bashore rebound, which goes through a minimum in the glass transition region, was obviously not observed.

Table 8. LOG (G'') VALUES (MPa) AT VARIOUS FREQUENCIES (RAD/SEC) FROM THE ROOM TEMPERATURE REFERENCE MASTER CURVES

Sample	10^2	10^4	10^6	10^8	10^{10}
1	5.68	6.44	6.88	7.17	7.45
4	5.02	5.76	6.79	7.72	7.09
6	4.99	5.66	6.46	7.32	8.03
8	5.22	6.61	7.49	7.97	8.11
12	6.03	7.24	7.81	7.95	7.91
15	5.59	6.73	7.51	7.94	8.09
18	5.28	6.01	6.84	7.71	8.20
19	6.10	6.12	6.59	6.73	6.74
21	6.23	7.26	7.87	8.08	7.94
22	5.86	7.10	8.00	8.18	8.00
23	4.91	6.26	7.39	8.09	8.35
24	5.08	6.86	7.83	7.96	7.59
25	6.74	7.12	7.78	8.40	8.64

CONCLUSIONS

A number of chemically dissimilar polymers have been evaluated as shock absorbing materials. This involved examining several classes of soft polyurethane elastomers prepared in the laboratory and comparing their properties with those of several commercial shock absorbing polymers. Glass transition temperatures of the polymers ranged from -68°C to -19°C. Final softening temperatures ranged from 115°C to 246°C.

Stress-strain measurements revealed that most of the polymers are weak, exhibiting tensile strengths in the range 0.7 MPa to 20.7 MPa. If large deformations are associated with the actual shock absorbing application, this energy to break the material becomes an important parameter for impact behavior. Chemical similarity in chain extender was associated with similar elongation to break.

All of the polymers were evaluated by Bashore rebound from -40°C to 20°C , the objective being to find low resilience throughout the temperature range tested. Three of the experimental materials exhibited this low Bashore behavior, as did three of the commercial polymers. Phase mixing in the experimental materials determined where the T_g of the material occurred and, thus, the minimum temperature for Bashore rebound. The Bashore results suggest that a polyol mixture in the polyurethane may lower the rebound across the temperature range of interest.

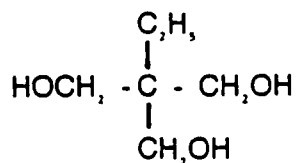
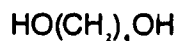
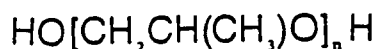
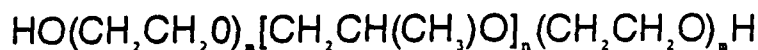
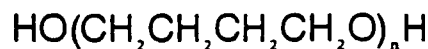
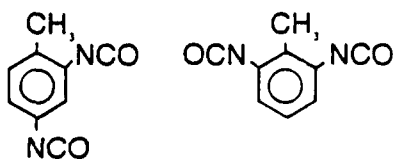
Dynamic mechanical analysis data obtained between 0.1 rad/sec and 100 rad/sec were shifted to obtain estimates of the moduli of the materials at high frequency. $\tan \delta$ values at approximately 1000 rad/sec were found to have the best qualitative agreement with the Bashore rebound results at room temperature. However, impact rates of interest most likely correspond to frequencies much higher than this. Room temperature reference shifted data indicate maxima in $\tan \delta$ at approximately 10^8 rad/sec for polymers with glass transition temperatures of approximately -60°C by standard techniques. When a lower reference temperature is used, the $\tan \delta$ peak is shifted to lower frequencies, effectively lowering the $\tan \delta$ value and the corresponding impact properties in the frequency range of interest.

Polyol structure was observed as an important parameter in the dynamic mechanical behavior of the polymers in this study. A PTMO-based material showed low $\tan \delta$ values over the frequency range investigated and corresponding good rebound. Lower polyol molecular weight led to more phase mixing and corresponding lower frequency $\tan \delta$ maxima. Slightly higher frequency maxima were obtained for a sulfur containing polyol when compared to PPG-based materials at similar molecular weights with ethylene oxide end-capped PPG slightly higher than pure PPG. The potential gain in shifting the $\tan \delta$ maxima to higher frequencies with the sulfur containing polyol may be offset by somewhat lower $\tan \delta$ values.

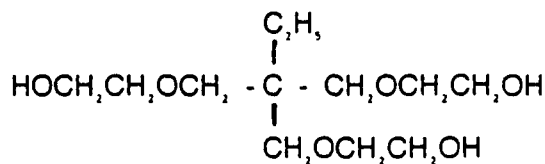
Higher frequency $\tan \delta$ maxima were obtained for the synthesized polymers with lower $\tan \delta$ values than the commercial materials. However, good impact at low temperatures and the frequencies of interest may not be met by the polymers in this study. Polymers with broader and lower glass transition temperature regions must be sought to meet this requirement. Testing of shock absorbing polymers under actual application conditions is also recommended for an accurate assessment of impact behavior.

ACKNOWLEDGMENTS

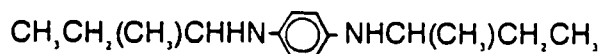
The authors would like to thank Richard Matton for preparing the polyurethanes, Karim Gabriel for assistance with the dynamic mechanical analysis, and Alexander Chin for thermal analysis measurements.



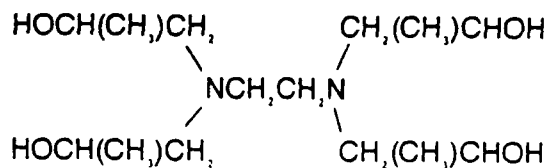
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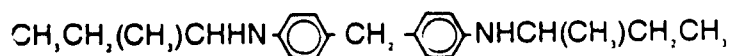
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QUADROL



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Figure 1. The structures of the chemical compounds used to prepare the polyurethanes.

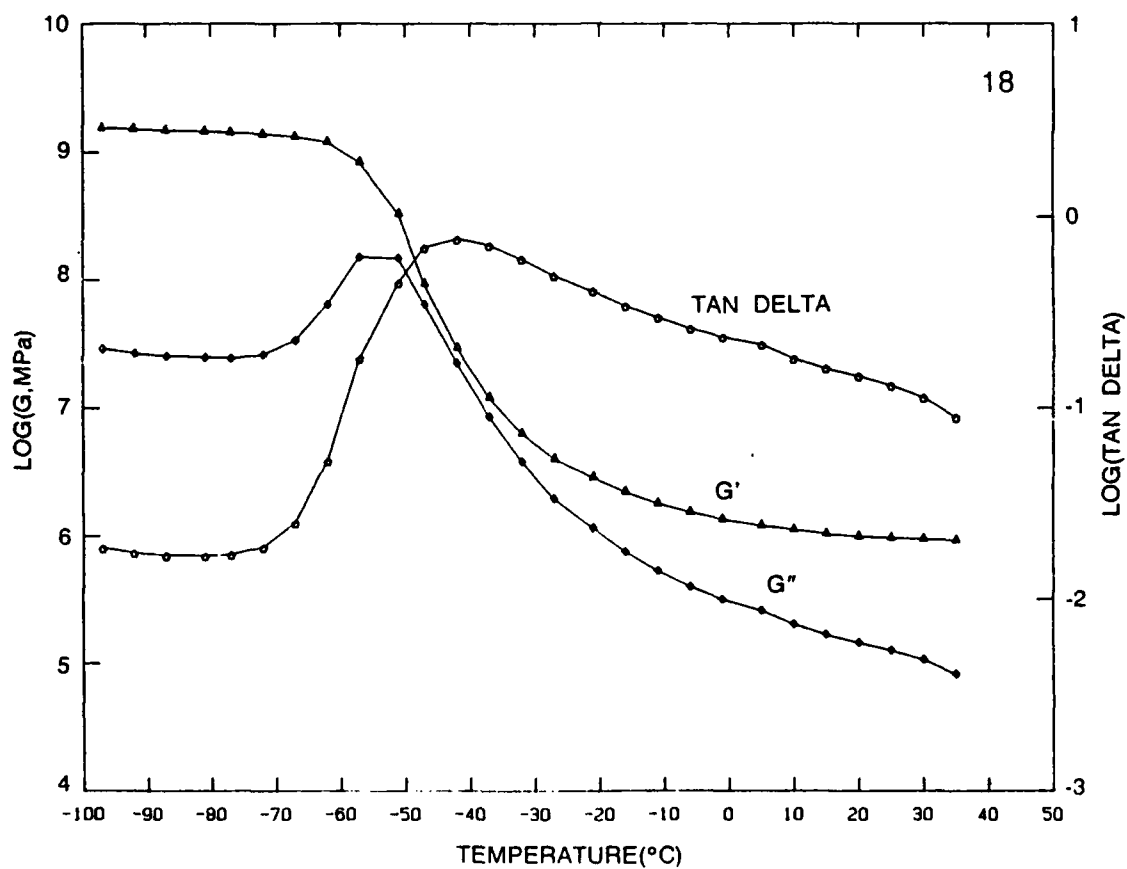


Figure 2. Dynamic mechanical analysis of Sample 18 showing G' , G'' , and $\tan \delta$ from 100°C to 50°C at 10 rad/sec.

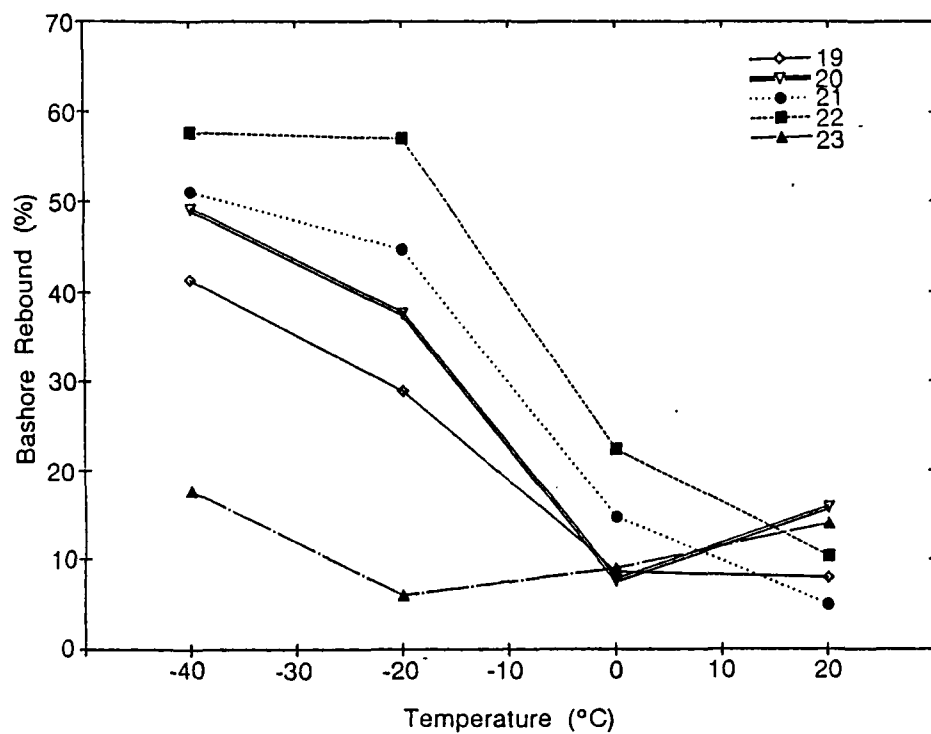


Figure 3a. Bashore rebound curves for Samples 19, 20, 21, 22, and 23.

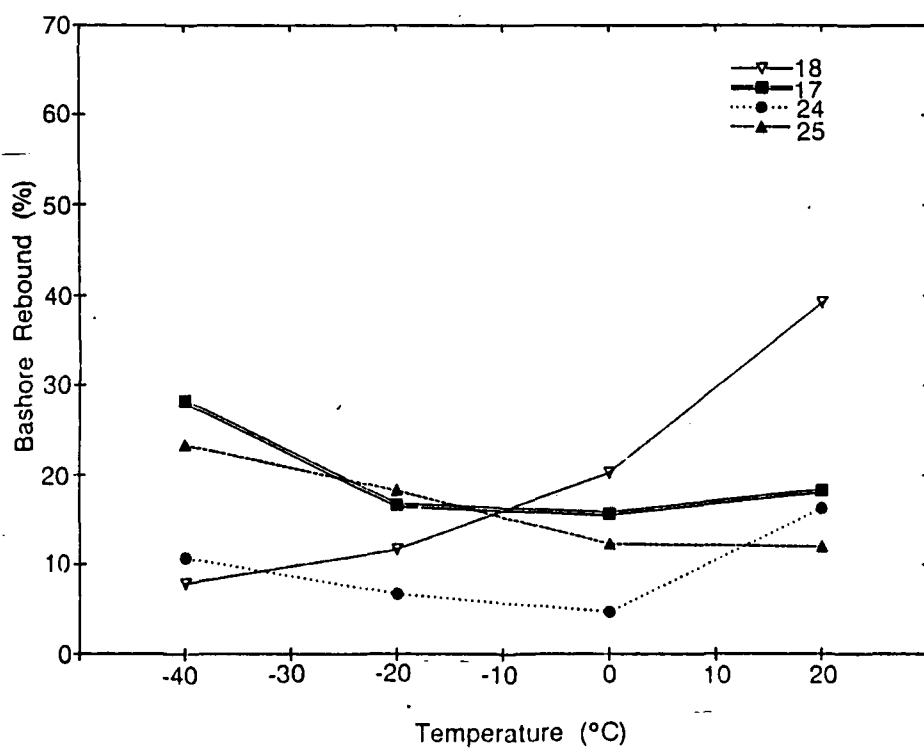


Figure 3b. Bashore rebound curves for Samples 17, 18, 24, and 25.

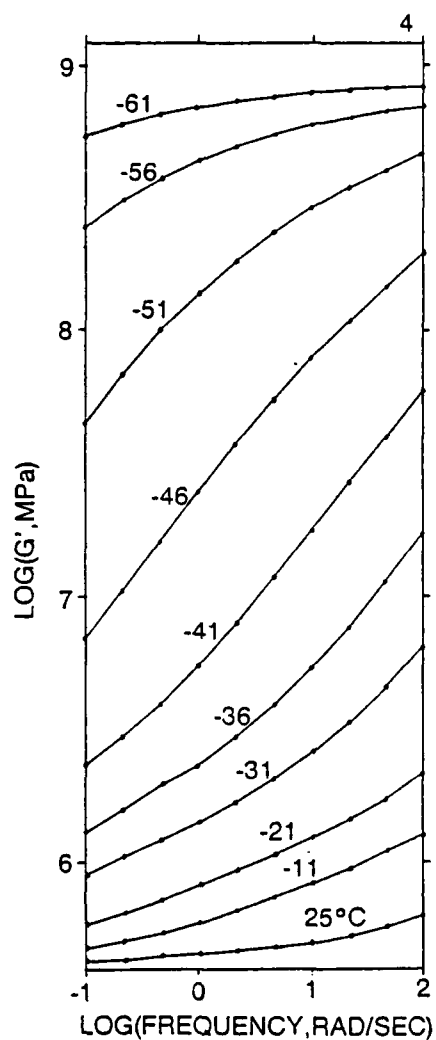


Figure 4a. Storage modulus data of Sample 4 obtained at 0.1 rad/sec to 100 rad/sec at a series of temperatures.

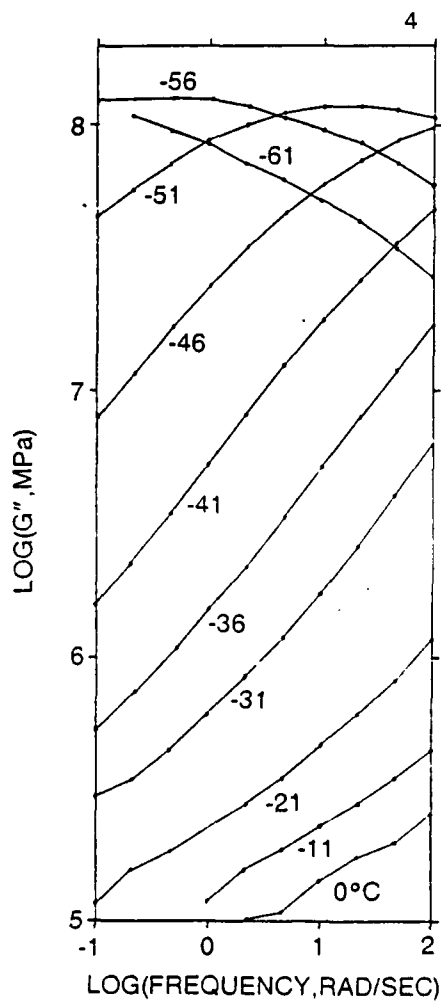


Figure 4b. Loss modulus master curve for Sample 4 with a room temperature reference.

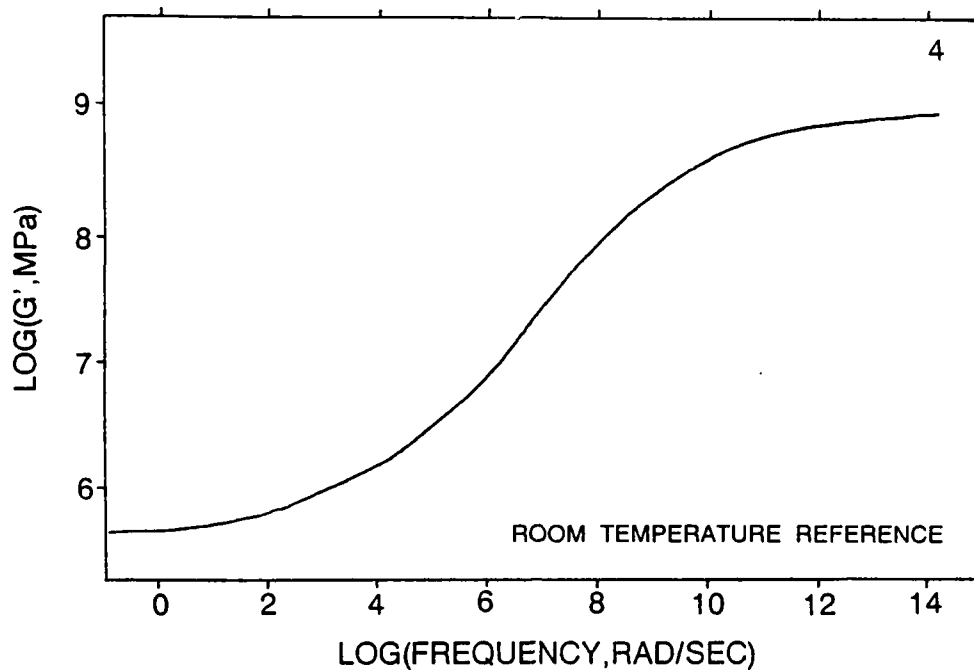


Figure 5a. Storage modulus master curve for Sample 4 with a room temperature reference.

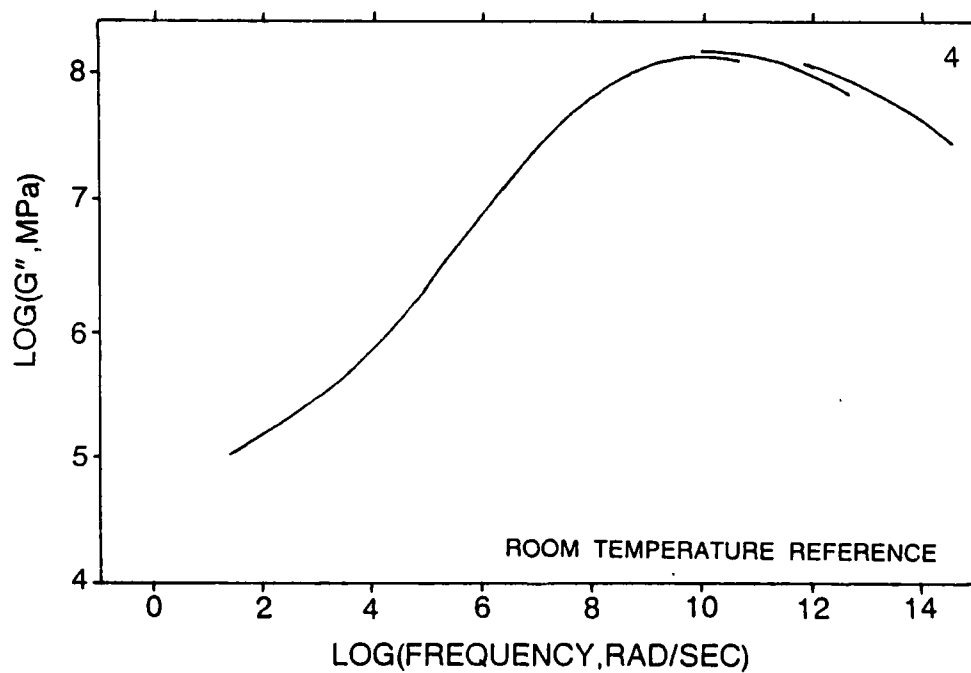


Figure 5b. Loss modulus master curve for Sample 4 with a room temperature reference.

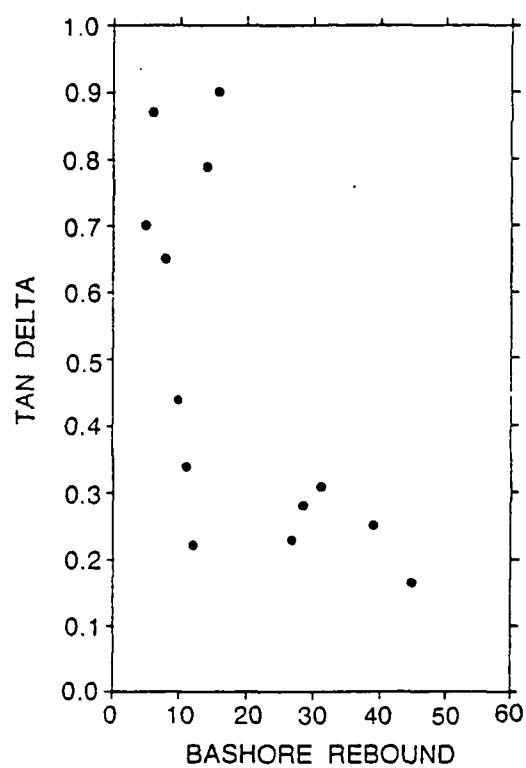


Figure 6. $\tan \delta$ at 1000 rad/sec with a room temperature reference versus Bashore rebound at 20°C.

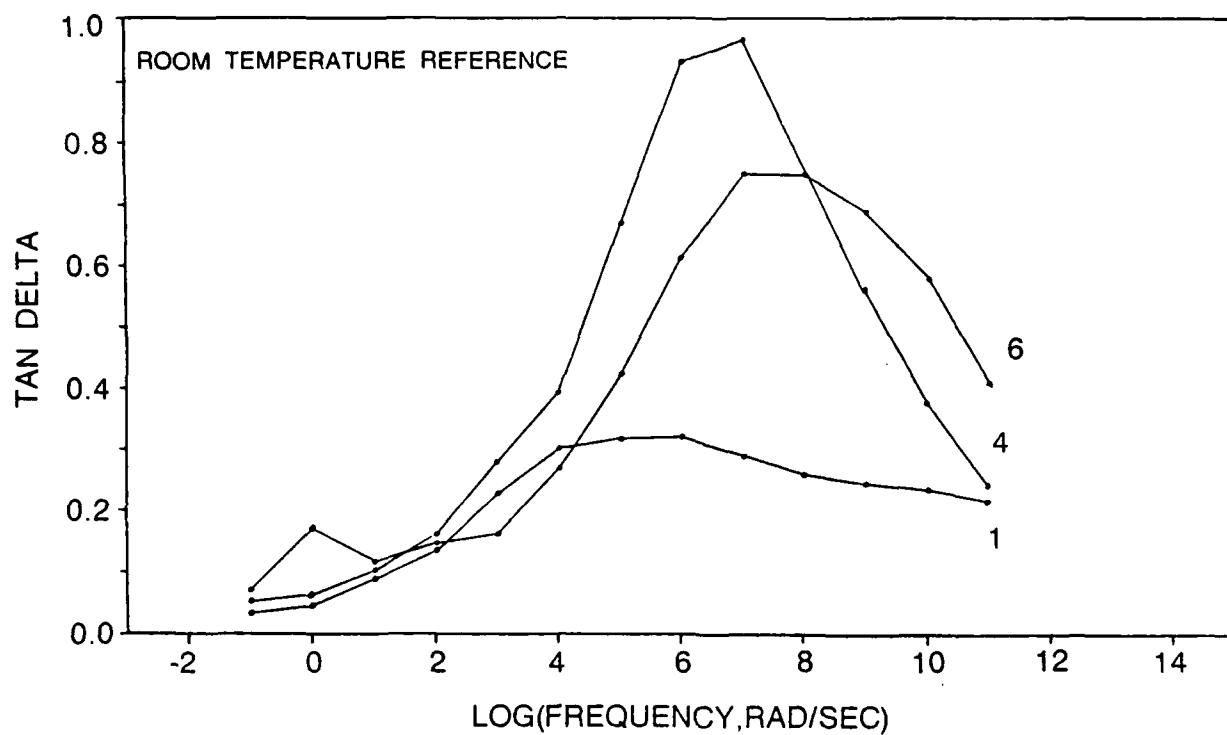


Figure 7. $\tan \delta$ versus frequency with a room temperature reference for Samples 1, 4, and 6.

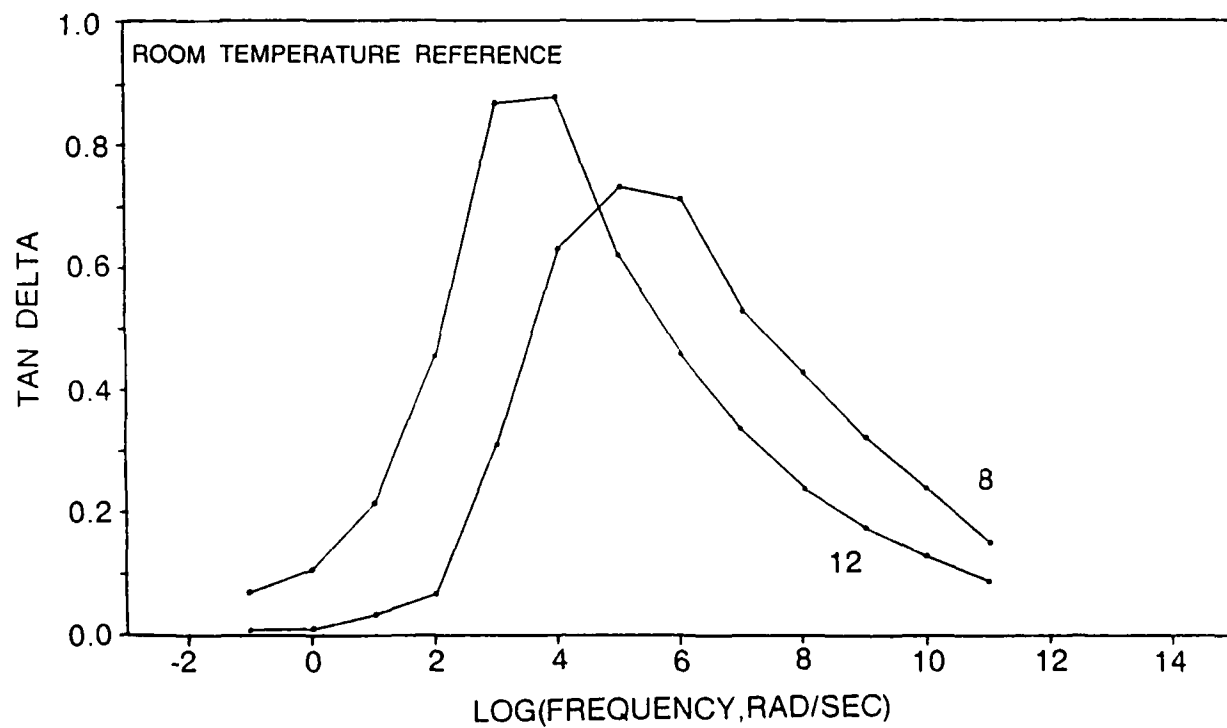


Figure 8. $\tan \delta$ versus frequency with a room temperature reference for Samples 8 and 12.

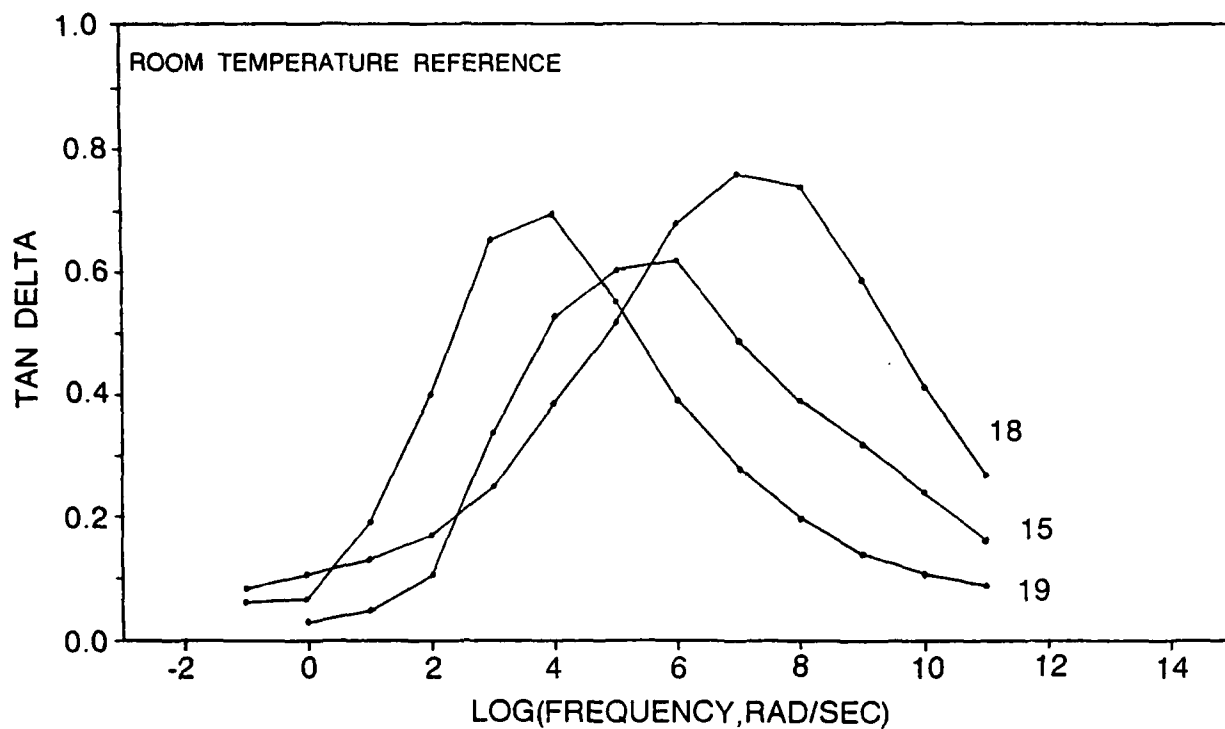


Figure 9. $\tan \delta$ versus frequency with a room temperature reference for Samples 15, 18, and 19.

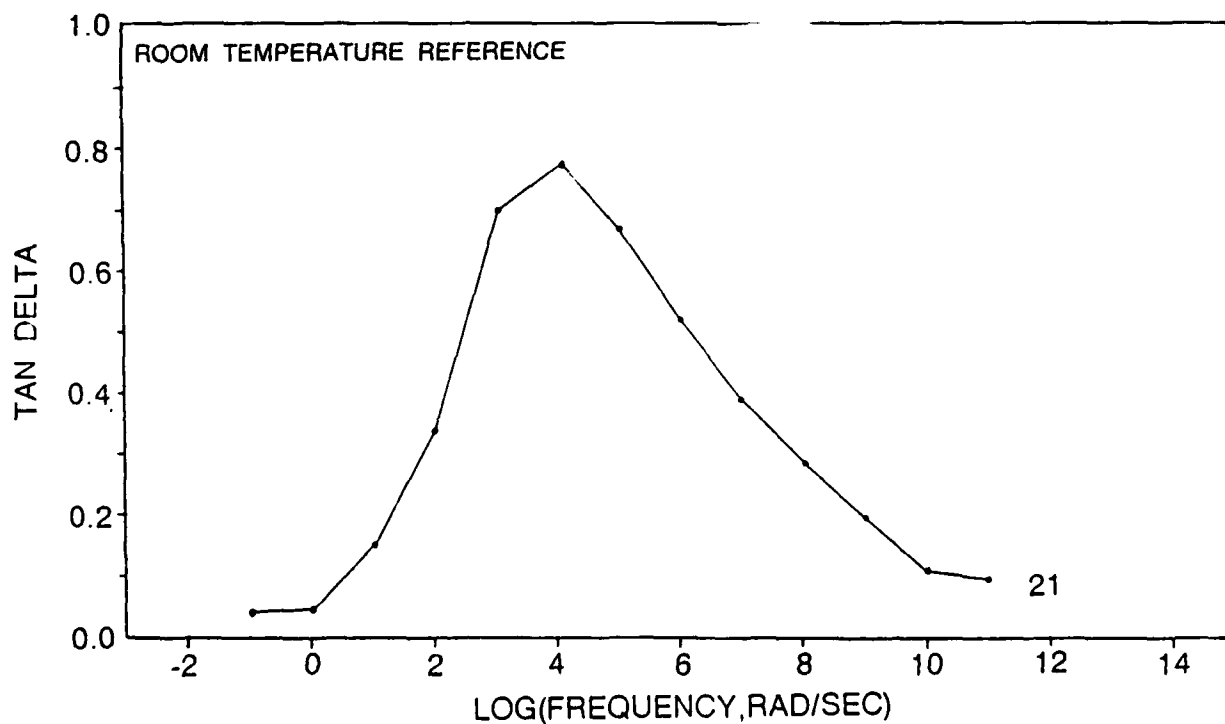


Figure 10. $\tan \delta$ versus frequency with a room temperature reference for Sample 21.

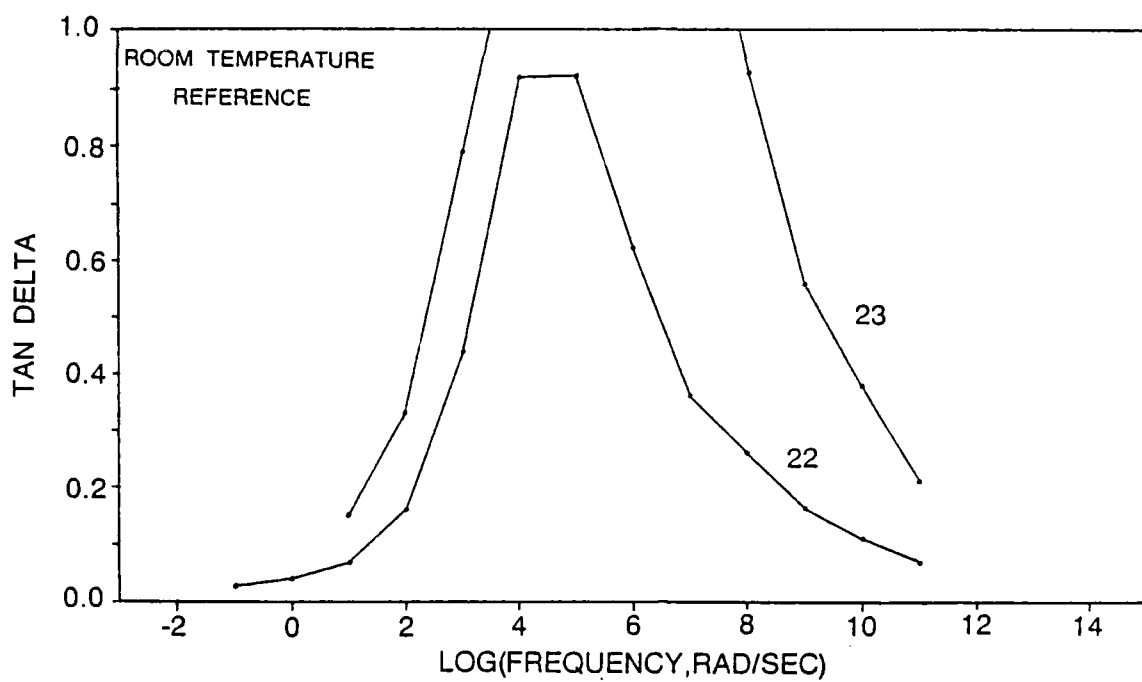


Figure 11. $\tan \delta$ versus frequency with a room temperature reference for Samples 22 and 23.

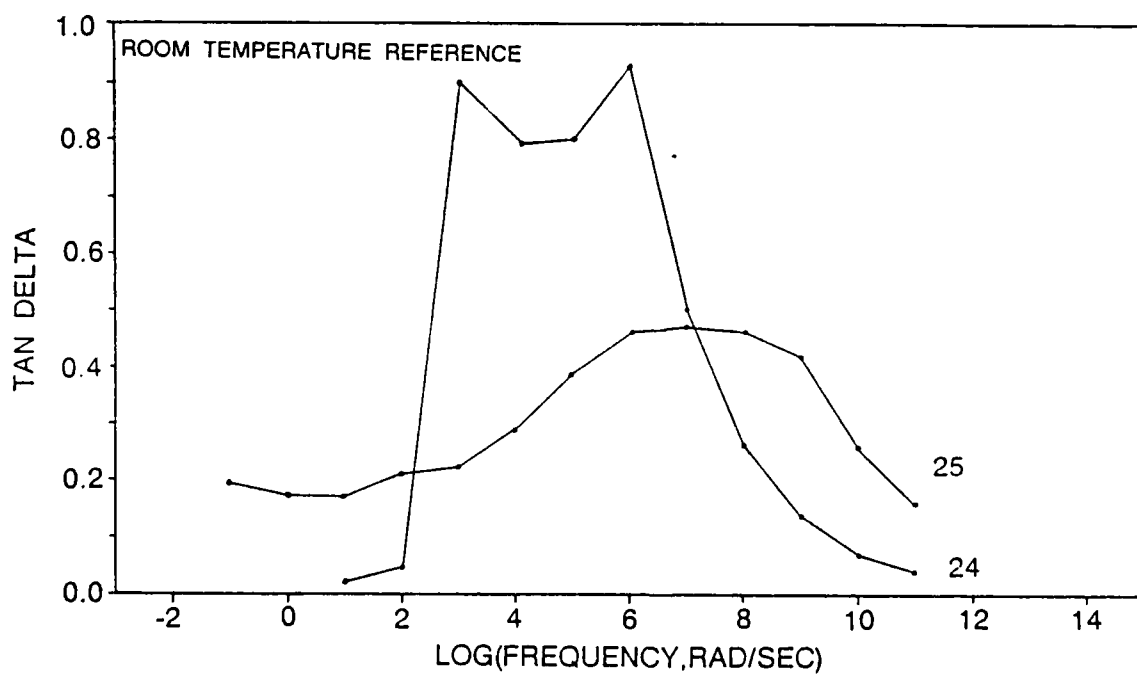


Figure 12. $\tan \delta$ versus frequency with a room temperature reference for Samples 24 and 25.

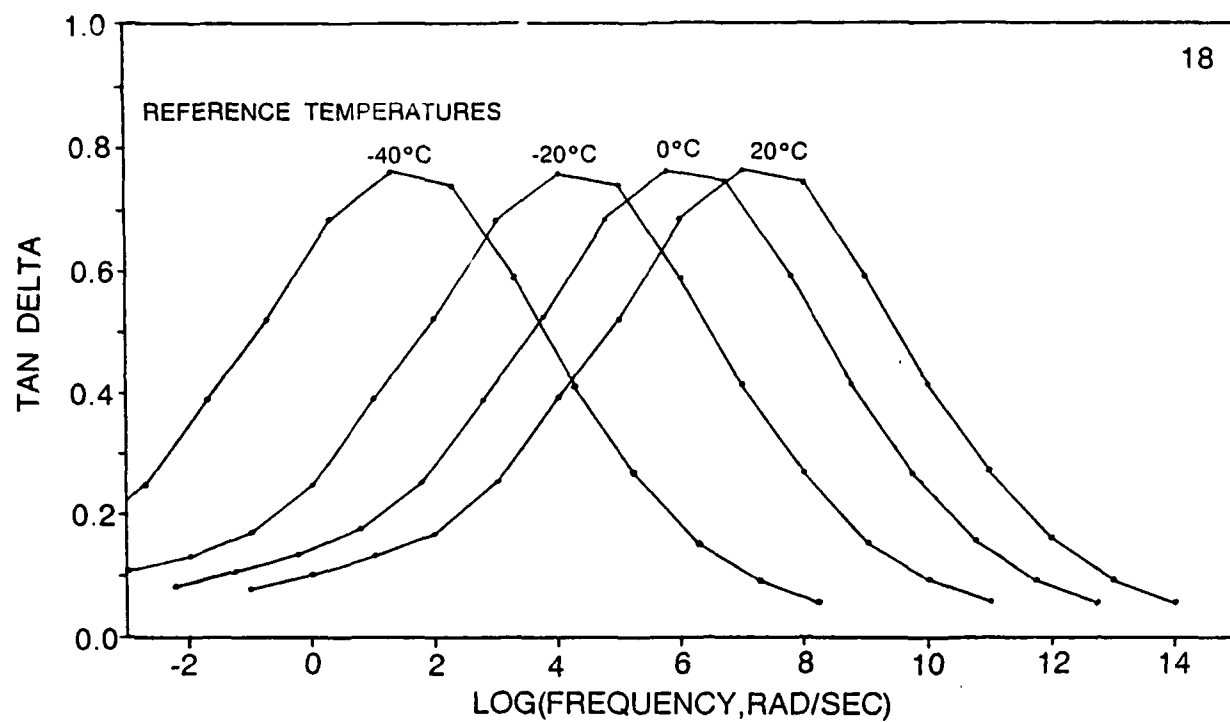


Figure 13. Tan δ versus frequency with reference temperatures of -40°C, -20°C, 0°C, and 20°C for Sample 18.

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<p>U.S. Army Materials Technology Laboratory Watertown, Massachusetts 02172-0001</p> <p>STUDIES OF POLYMERS FOR SHOCK ABSORPTION APPLICATIONS</p> <p>Catherine A. Byrne and Walter X. Zukas</p> <p>Technical Report MTL TR 91-21, May 1991, 27 pp- illus-tables.</p> <p>The purpose of this study was to evaluate polymers with potential shock damping properties. Many soft polyurethane elastomers were prepared in the laboratory and evaluated by thermal and mechanical analysis; these include mostly poly(propylene oxide) and polythioether-based elastomers prepared with toluene diisocyanate. Tri- and tetrafunctional chain extenders were used in all cases, as well as some unusual secondary diamines. The objective was to soften the polymers, disorganize the hard phase, and broaden the soft segment glass transition temperature while still allowing a rather broad use temperature. Comparisons were made to commercially available shock absorbing polymers. The synthesis of the polyurethanes is discussed in detail and the results of characterization of all of the polymers are described. The polymers exhibit Tg's ranging from -68°C to -19°C, final softening temperatures between 115°C and 246°C, Shore A hardness values ranging from 13 to 87, tensile strengths of 0.7 MPa to 20 MPa and elongations of 175% to 2900%. Several display low Bashore rebound values in the temperature range of interest. Dynamic mechanical data were extrapolated to high frequency through the assembly of master curves and revealed that the polymers evaluated probably would exhibit good high frequency shock absorbing properties at room temperature or somewhat above room temperature, but that they would not display satisfactory behavior at temperatures significantly below room temperature.</p>	<p>AD <u>UNCLASSIFIED</u> UNLIMITED DISTRIBUTION</p> <p>Key Words Polyurethane Elastomer Damping</p>
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